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13. ABSTRACT (Maximum 200 words) The goal of our research was to prepare decafluoroferrocene and decafluororuthenocene from permetalated precursors, to prepare mono- and disubstituted perfluorometallobenes, and to prepare and evaluate the thermal characteristics of polymers and oligomers derived from the perfluorometallobenes. In the period of support, we explored the preparation of permercurated, perlithiated, permagnesiased, perzincated, and peraluminated cyclopentadienyl complexes and examined the reactions of these species with simple electrophiles. The motivation for working with the permetalated metallobenes has been the finding that permercurated metallobenes cannot be fluorinated to give decafluorometallobenes. Most fluorinating agents are not strong enough to react with the permercurated metallobenes, while very strong fluorinating agents destroy the metallobenes. We reasoned that more reactive carbon-metal bonds would require less reactive fluorinating agents, which might lead to a successful preparation of decafluorometallobenes. Despite many attempts, it has so far not been possible to find that right combination of permetalated metallobene and electrophilic fluorinating agents that gives the perfluorometallobene.					
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1. Cover Sheet

Final Technical Report (1/93-12/95)

**"Synthesis and Properties of Perfluoroferrocene and Perfluororuthenocene.
A Potential Class of High Temperature Materials"**

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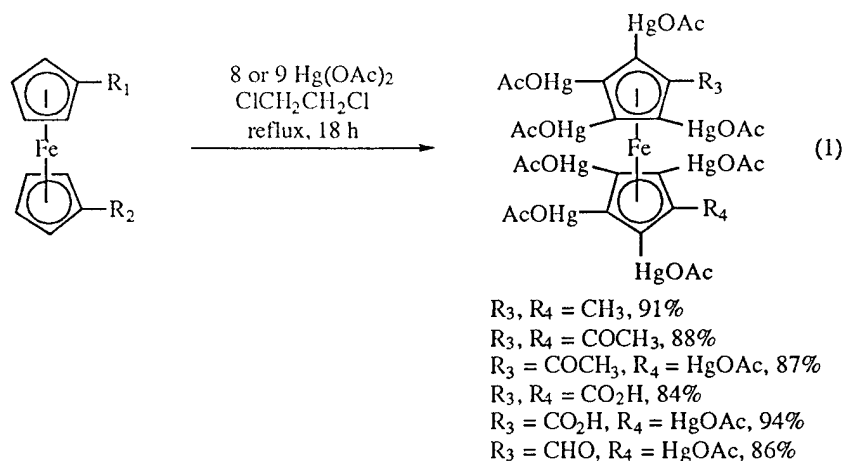
2., 3. Objectives/Status of Effort

The goal of our research was to prepare decafluoroferrrocene and decafluororuthenocene from permetalated precursors, to prepare mono- and disubstituted perfluorometallocenes, and to prepare and evaluate the thermal characteristics of polymers and oligomers derived from the perfluorometallocenes. In the period of support, we explored the preparation of permercurated, perlithiated, permagnesiased, perzincated, and peraluminated cyclopentadienyl complexes and examined the reactions of these species with simple electrophiles. The motivation for working with the permetalated metallocenes has been the finding that permercurated metallocenes cannot be fluorinated to give decafluorometallocenes. Most fluorinating agents are not strong enough to react with the permercurated metallocenes, while very strong fluorinating agents destroy the metallocenes. We reasoned that more reactive carbon-metal bonds would require less reactive fluorinating agents, which might lead to a successful preparation of decafluorometallocenes. Despite many attempts, it has so far not been possible to find that right combination of permetalated metallocene and electrophilic fluorinating agents that gives the perfluorometallocene.

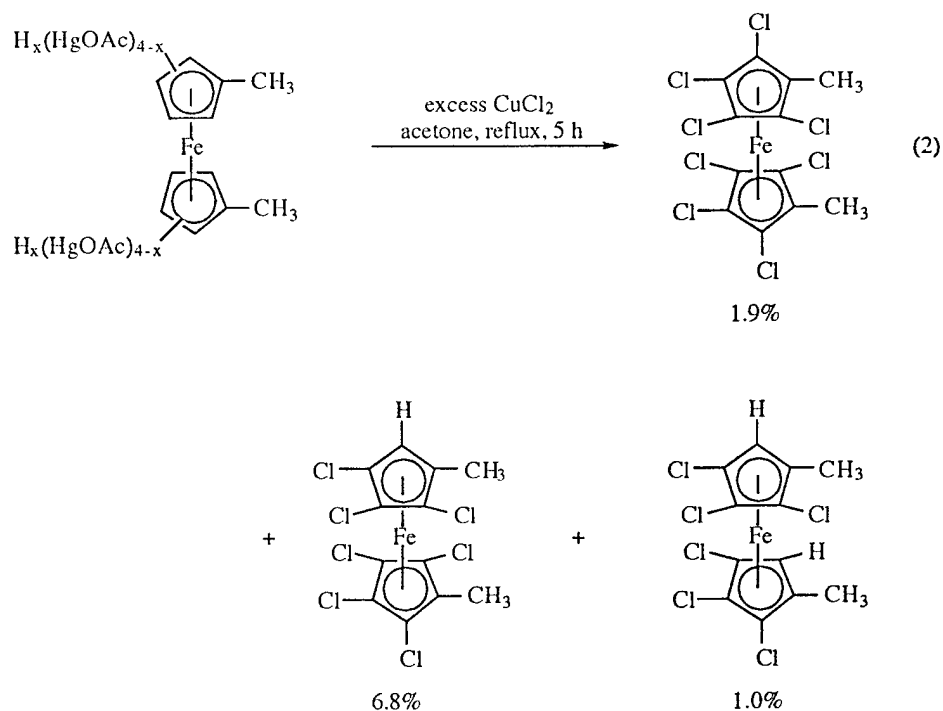
4. Accomplishments/New Findings

Work Performed

Mercuration of Ferrocene and Substituted Ferrocenes.^{1,2} Treatment of the six mono- and disubstituted ferrocenes with nine and eight equivalents of mercuric acetate, respectively, in refluxing 1,2-dichloroethane for 18 h afforded the mercurated ferrocenes as yellow to orange insoluble powders that precipitated from the reaction media (eq 1). Yields ranged between 84-94%, assuming a permercurated formulation. The products were insoluble in all common organic solvents, which precluded analysis by solution NMR methods. The ferrocenes were characterized by melting points, microanalyses, and IR spectroscopy. The carbon and hydrogen microanalyses hovered around the values calculated for the permercurated compounds, but could not be obtained within $\pm 0.4\%$. In addition, the calculated carbon and hydrogen contents were not strongly dependent on the degree of mercuration (e.g., Anal. calcd. for $C_{10}(HgOAc)_8(CH_3)_2Fe$: C, 14.73; H, 1.32. Calcd for $C_{10}H_2(HgOAc)_6(CH_3)_2Fe$: C, 16.32; H, 1.48). Hence, the above data could not conclusively establish the degree of mercuration.



Halogenation reactions were addressed as a method to probe the degree of mercuriation in the mercurated ferrocenes. However, treatment with cupric chloride in acetone, cupric bromide in acetone, or potassium tribromide in water/methanol (conditions we have previously used to replace mercury by halogen⁷) afforded deep green solutions indicative of ferrocene oxidation. Only with the dimethylferrocene system was it possible to isolate any halogenated ferrocenes in pure form. In order to obtain enough product for careful characterization, the chlorination was conducted on a large scale (ca. 2.0 mmol) using cupric chloride (eq 2). Chlorination under these conditions afforded an inseparable 20:70:10 mixture of 1,1',2,2',3,3',4,4'-octachloro-5,5'-dimethylferrocene (1.9%), 1,1',2,2',3,3',4-heptachloro-5,5'-ferrocene (6.8%), and 1,1',2,2',3,3'-hexachloro-5,5'-ferrocene (1.0%). In addition, four other unidentified chlorinated ferrocenes were observed, although they constituted ≤ 5 mol % of the chlorinated ferrocene mixture. The identity and distribution were established by a combination of GLC, GLC/MS, and ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR analyses. The principal identification was by GLC/MS. These chlorinated ferrocenes showed molecular ions under electron impact conditions, with observed isotope distributions for the molecular ion envelope that were identical to the calculated patterns. Bromination using cupric bromide yielded a mixture of brominated ferrocenes in similar yields as those derived from cupric chloride.

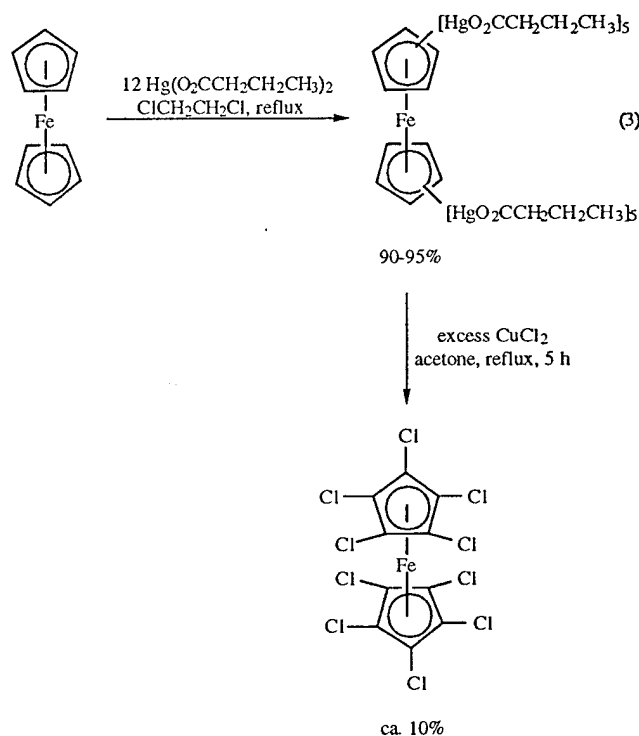


In order to determine if the mercurated dimethylferrocene could be obtained as the pure octamercurated compound, the mercuration of 1,1'-dimethylferrocene was repeated using 12 equiv of mercuric acetate and a reflux time of 24 h. Workup afforded an orange powder in 93% yield. Chlorination of this material using the conditions described above yielded a mixture of 1,1',2,2',3,3',4,4'-octachloro-5,5'-dimethylferrocene (1.3% isolated yield), 1,1',2,2',3,3',4'-heptachloro-5,5'-ferrocene (5.3% isolated yield), and five other minor ferrocene products ($\leq 0.3\%$ yield). Thus, neither the yield of chlorinated ferrocenes nor the ratio was substantially affected by using excess mercuric acetate and a longer reflux.

The chlorination and bromination of the mercurated dimethylferrocene yielded similar product mixtures consisting of 20-22% octahalodimethylferrocene, 70-74% heptahalodimethylferrocene, and 4-10% of hexahalodimethylferrocene. We have previously reported that analogous halogenation reactions of decakis(acetoxymercurio)ruthenocene and decakis(acetoxymercurio)osmocene proceed without detectable incorporation of hydrogen into the products. Accordingly, it is a reasonable assumption that the observed halogenation mixtures represent the mixture of mercurated ferrocenes present in the mercurated dimethylferrocene. We suggest, based upon the halogenation results, that the mercurated dimethylferrocene is a mixture of about 20% octakis(acetoxymercurio)dimethylferrocene, 70% heptakis(acetoxymercurio)-dimethylferrocene, and 10% hexakis(acetoxymercurio)dimethylferrocene. The calculated carbon and hydrogen contents for such a mixture (Calcd: C, 15.38; H, 1.38. Found: C, 15.72; H, 1.57)

are much closer to the experimentally observed values than those calculated for pure octakis(acetoxymercurio)dimethylferrocene.

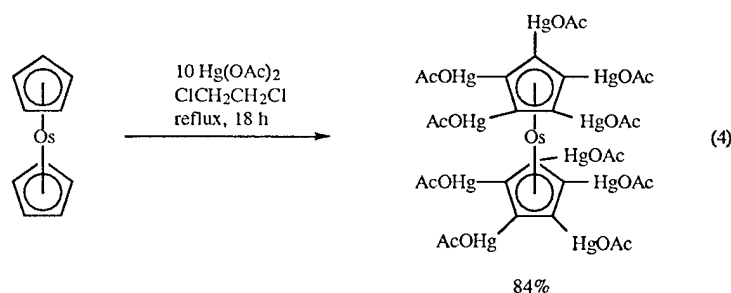
In view of the problems associated with the mercuration of the substituted ferrocenes with mercuric acetate, the decamercuration of ferrocene was reexamined. Treatment of ferrocene with mercuric acetate (10 equiv) in refluxing 1,2-dichloroethane afforded an insoluble orange precipitate of mercurated ferrocene. Chlorination of this material led to ca. 30% yields of octachloroferrocene, nonachloroferrocene, and decachloroferrocene in an approximate 20:60:20 ratio, as determined by GLC/MS. Thus, ferrocene cannot be decamercurated under conditions used to decamercurate ruthenocene and osmocene (*vide infra*). We reasoned that the polymercurated ferrocenes were probably extremely insoluble and precipitated from the reaction medium prior to complete mercuration. Therefore, ferrocene was treated with mercuric butyrate under conditions otherwise similar to the above to afford decakis(butyroxymercurio)ferrocene (90-95%) as a bright orange solid (eq 3). Chlorination of using cupric chloride in refluxing acetone gave decachloroferrocene in ca. 10% yield as the sole product, as determined by GLC analysis.



Mercuration of Ruthenocene and Substituted Ruthenocenes.³⁻⁵ We have reported that the cyclopentadienyl hydrogens in pentamethylruthenocene, ruthenocene, and pentamethylindenylruthenocene can be completely replaced by acetoxymercurio groups upon treatment of the metallocenes with the appropriate number of equivalents of mercuric acetate. The degree of mercuration was established by a combination of spectroscopic methods, analytical

techniques, and halogenation studies. Unfortunately, all attempts to fluorinate the carbon-mercury bonds failed, due to the low reactivity of the carbon-mercury bonds. Strong electrophilic fluorinating agents gave complete destruction of the ruthenocenes, while mild electrophilic fluorinating agents either did not react at all or did not react completely. The permercuration of ferrocene with mercuric trifluoroacetate or mercuric acetate was also investigated.⁵ Both mercurating agents gave mixtures of polymercurated ferrocenes in which the decamercurated species was present, along with substantial amounts of the nonmercured and octamercurated ferrocenes. Decachloroferrocene could be isolated in 27% yield by column chromatography, followed by crystallization from hexane.

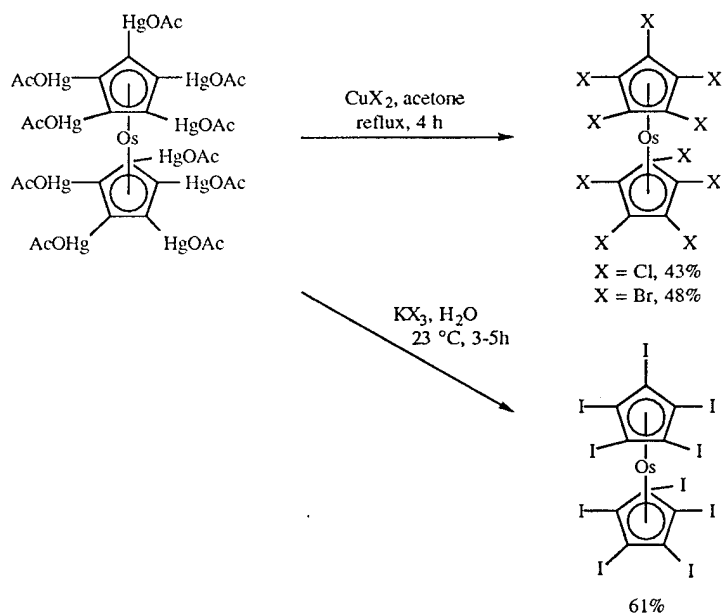
Mercuration of Osmocene.⁶ Treatment of osmocene with mercuric acetate (10 equiv) in refluxing 1,2-dichloroethane for 18 h afforded decakis(acetoxymercurio)osmocene (84%) as a white solid that precipitated from the reaction medium (eq 4). The decamercurated osmocene was insoluble in all common organic solvents, which precluded analysis by solution NMR methods. It was characterized by melting point, microanalysis, and IR spectroscopy. The C, H microanalysis results were consistent with a decamercurated formulation. The infrared spectrum of 1 showed absorptions at 1564 (vs), 1402 (s), 1331 (m), 1040 (w), 1014 (m), 917 (w), 684 (m), 646 (m), and 613 (m) cm^{-1} . For comparison, mercuric acetate showed strong absorptions at 1555, 1400, 1330, and 653 cm^{-1} . Despite the acceptable microanalysis results, it was not possible to assign confidently a decamercurated structure, since the calculated microanalytical values were not strongly dependent on the degree of mercuration (e.g., Anal. Calcd: C, 12.40; H, 1.04. Anal. Calcd for octamercurated osmocene: C, 13.07; H, 1.10).



The fully mercurated nature was confirmed by its reaction with halogenating agents (Scheme 1). Treatment with cupric chloride (ca. 50 equiv) in refluxing acetone for 4 h afforded decachloroosmocene (43%) as white crystals, after workup. Decachloroosmocene was readily soluble in chloroform and dichloromethane and could be subjected to NMR analysis. The ^1H NMR of the crude product did not show any resonances in the δ 4-6 region, which demonstrates that the crude product contained $\leq 2\%$ of partially chlorinated osmocenes. This result also implied $\geq 98\%$ decamercuration. Analogous halogenations using cupric bromide in refluxing acetone or

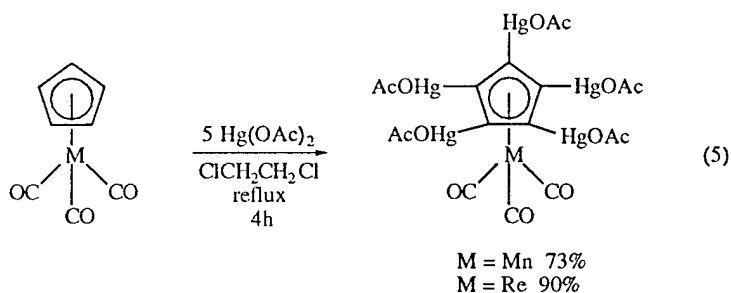
potassium triiodide in water/methanol afforded decabromoosmocene (48%) and decaiodoosmocene (61%) as white and yellow solids, respectively. The proposed structures based upon spectral and analytical data, and upon a crystal structure determination for decachloroosmocene. The $^{13}\text{C}\{^1\text{H}\}$ NMR data of were particularly revealing. A steady shielding of the carbons was observed in going from chloride to iodide substituents (decachloroosmocene, 86.20 ppm; decabromoosmocene, 78.41 ppm; decaiodoosmocene, 62.37 ppm). For comparison, the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of osmocene shows a singlet at 63.56 ppm in chloroform-d.

Scheme 1. Halogenation Studies



Mercuration of Cyclopentadienylmanganese Tricarbonyl and Cyclopentadienylrhenium Tricarbonyl.⁷ Treatment of cyclopentadienylmanganese tricarbonyl with mercuric acetate (5 equiv) in refluxing 1,2-dichloroethane for 4 h afforded penta(acetoxymercurio)cyclopentadienylmanganese tricarbonyl (73%) as a yellow powder (eq 5). This compound was slightly soluble in dichloromethane and could be obtained as an analytically pure powder by filtration and removal of the solvent. The ^1H NMR of the material showed no resonances between δ 3-6 that could be attributed to a partially mercurated complex, which indicates $\geq 98\%$ pentamercured. An experiment was conducted in which cyclopentadienylmanganese tricarbonyl was treated with mercuric acetate (1 equiv) under conditions otherwise identical to the above preparation. Workup afforded penta(acetoxymercurio)cyclopentadienylmanganese tricarbonyl (6%) and unreacted cyclopentadienylmanganese tricarbonyl (78%). This experiment indicates that the first mercuration step is the slowest. Analogous mercuration of cyclopentadienylrhenium tricarbonyl afforded

penta(acetoxymercurio)cyclopentadienylrhodium tricarbonyl (90%) as a pale yellow powder (eq 5).



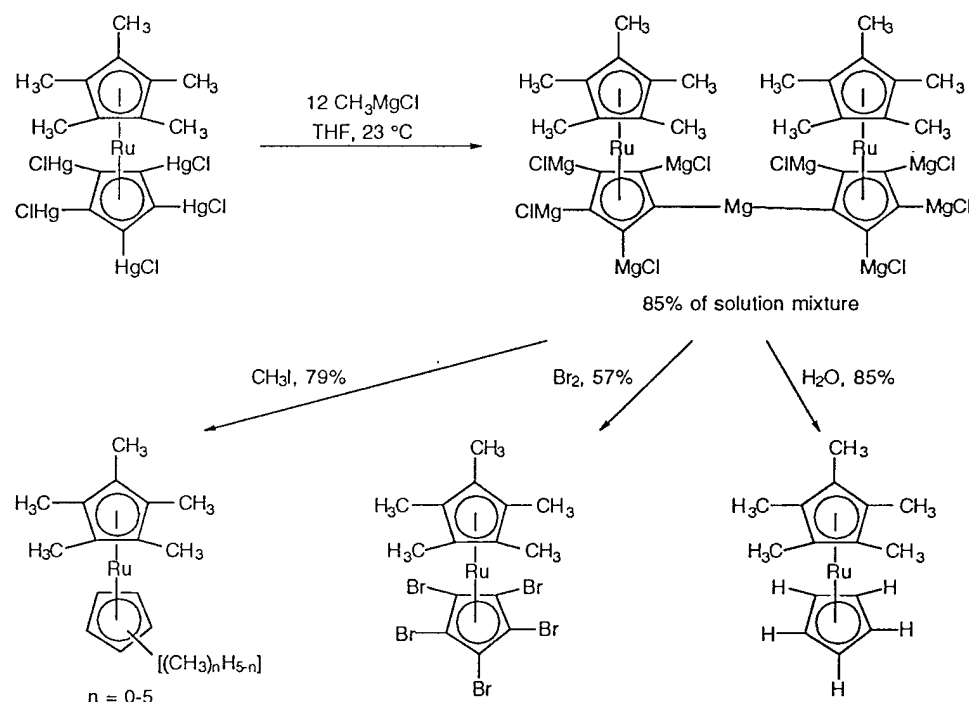
Treatment of penta(acetoxymercurio)cyclopentadienylmanganese tricarbonyl with excess cupric chloride (25 equiv) in refluxing acetone for 3 hours afforded pentachlorocyclopentadienylmanganese tricarbonyl (45%) as a yellow crystalline solid. Analogous treatment with cupric bromide afforded pentabromocyclopentadienylmanganese tricarbonyl (44%) as a yellow crystalline solid. Penta(acetoxymercurio)cyclopentadienylmanganese tricarbonyl was also halogenated using potassium triiodide (prepared from I_2 and KI at 25 °C) in water to afford pentaiodocyclopentadienylmanganese tricarbonyl (19%) as an orange crystalline powder. The crystal structure of pentaiodocyclopentadienylmanganese tricarbonyl was determined.

Pentalithiocyclopentadienyl Complexes.^{8,9} We have reported the syntheses of pentamethylpentalithioruthenocene and decalithioruthenocene as well as their reactions with the simple electrophiles water, bromine, and methyl iodide.⁸ A more extensive survey of electrophiles has revealed that formation of hydrogen-substituted products (i.e., pentamethylruthenocene and ruthenocene) is the predominant reaction process with most electrophiles (e.g., $ClSiMe_3$, $Me_3O^+BF_4^-$, XeF_2).⁹ Experiments using $THF-^1H_8$ and $THF-^2H_8$ suggest that the hydrogen source is the solvent, rather than the electrophile. Examination of organic products from the reaction by GLC and GLC/MS indicates that there are 4-5 new minor compounds produced in the reactions. GLC/MS suggests that the products are substituted tetrahydrofuran derivatives. Experiments are in progress to differentiate between radical, radical ion, and carbanion processes to account for the products. Regardless of the path by which hydrogen-substituted products are produced, it is likely that synthetic applications of perlithiated metallocenes will be limited to strong electrophiles with small steric profiles.

Pentamagnesiated Cyclopentadienyl Complexes.¹⁰ Treatment of pentakis(chloromercurio)(pentamethyl)ruthenocene with methylmagnesium chloride (12 equiv) in tetrahydrofuran at 23 °C for 1 h led to its dissolution, giving a clear yellow-orange solution

containing a pentamagnesiated pentamethylruthenocene (Scheme 2). Hydrolysis of this solution with H_2O afforded pentamethylruthenocene (85%), while D_2O quench gave pentamethylruthenocene (97%) with 87% deuterium content in the cyclopentadienyl ligand. Carbon-mercury bonds in ruthenocenes are stable to water under the reaction conditions, which supports a pentamagnesiated formulation and rules out structures containing carbon-mercury bonds. Addition of bromine gave pentabromopentamethyl-ruthenocene (57%). Additional evidence for a magnesiated species was obtained from reaction with methyl iodide, which gave a mixture of methylated ruthenocenes between pentamethylruthenocene and decamethylruthenocene (79% total yield). Grignard reagents are well known to react with alkyl iodides by electron transfer pathways.

Scheme 2. Preparation and Reactions of the Pentamagnesiated Ruthenocene



Given the likelihood that a pentamagnesiated ruthenocene was being formed, we sought to characterize this species by spectroscopic methods. Treatment of pentakis(chloromercurio)(pentamethyl)ruthenocene with methylmagnesium chloride (12 equiv) in tetrahydrofuran- d_8 at ambient temperature, followed by ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR analysis, revealed 85% of a major product with a ^1H NMR resonance for the Cp^* ligand at δ 2.06 and 15% of at least five minor products with Cp^* resonances at δ 2.13, 2.12, 2.11, 2.10 and 2.08. No cyclopentadienyl C-H bonds were observed in the ^1H NMR spectrum, indicating that the magnesiated ruthenocenes contained $\leq 2\%$ of hydrogen on the cyclopentadienyl ligands. The

$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the dimeric ruthenocene showed resonances due to the Cp^* ligand at 84.40 ($\text{C}-\text{CH}_3$), and 16.32 ($\text{C}-\text{CH}_3$) ppm. Resonances from the magnesiated cyclopentadienyl ligand were observed at 123.35, 121.78, and 118.67 ppm, with intensities of approximately 2:1:2. A reasonable structure that is consistent with all of the data is a dimer with eight terminal chloromagnesio groups and one diruthenocenylmagnesium unit. The ipso-carbons in phenyl magnesium halides and diphenylmagnesium are found to resonate about 30-35 ppm downfield from benzene. The positions of the magnesiated carbon resonances (34.27-38.95 ppm downfield from $\text{C}-\text{CH}_3$) are thus appropriate for an aromatic magnesium compound. The minor compounds could not be identified due to their low concentrations, but are probably higher oligomers.

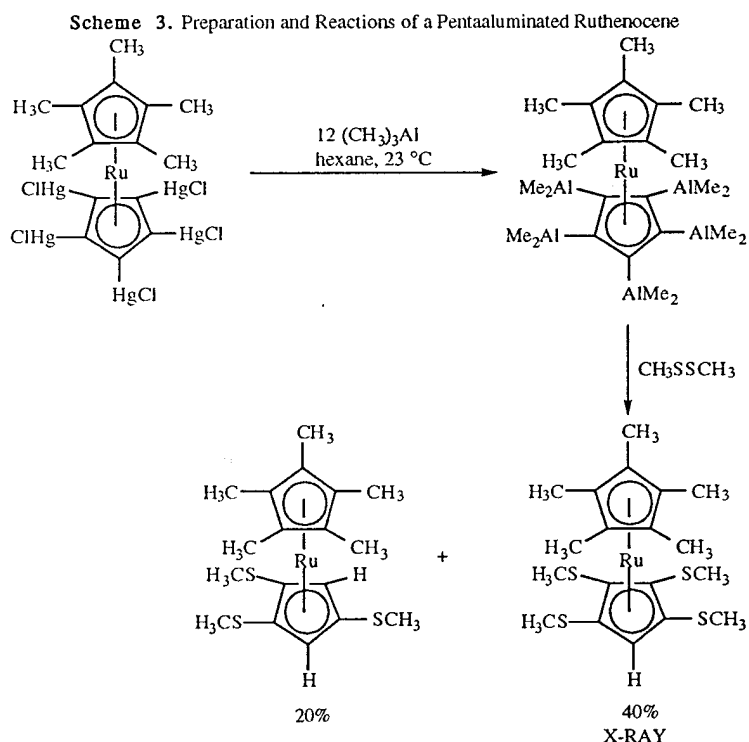
The isolation of the pentamagnesiated ruthenocene was attempted. A tetrahydrofuran solution prepared as above was treated with a large excess of hexane, resulting in the precipitation of a yellow-ochre powder. Analysis of the powder by ^1H NMR spectroscopy in tetrahydrofuran- d_8 revealed at least 12 broad Cp^* methyl resonances between δ 2.13-1.81, of which 2 (δ 2.06) was a minor component. It was not possible to obtain a $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum with sufficient signal to noise to allow structural assignments, due to the low concentration of each of the components. However, we propose that the isolated material corresponds to a mixture of oligomers that results from elimination of magnesium chloride from the dimer. This mixture is further evidence of the tendency of pentamagnesiated ruthenocenes to form oligomers. Infrared spectroscopy suggested that tetrahydrofuran was associated with the isolated powder, but the exact amount could not be assigned by the ^1H NMR spectrum because of residual hydrogen content in the tetrahydrofuran- d_8 . The reactivity of the isolated powder was similar to that of the compound generated in solution. Hydrolysis afforded pentamethylruthenocene (65%), while bromination with bromine gave pentabromopentamethylruthenocene (54%) and tetrabromopentamethylruthenocene (13%).

Decakis(chloromagnesio)ruthenocene was prepared by a similar route and was characterized by hydrolysis, bromination, and methylation.

Several significant inferences can be made from the above results. First, and perhaps most surprising, is that ruthenocenes bearing pentamagnesiated cyclopentadienyl ligands are stable and can be easily isolated and manipulated at ambient temperature. The complexes described herein are substantially more robust than the perlithiated analogs we described earlier, implying that permagnesiated aromatic compounds and permetalated aromatic compounds containing other main group metals will exhibit similar or possibly higher thermal stability. Such stability contradicts conventional wisdom, which would predict that placement of adjacent electropositive metals on aromatic molecules should be extremely unfavorable due to repulsion between the carbanionic sites. Second, NMR spectroscopy suggests that the permagnesiated ruthenocenes exist preferentially as dimers or higher oligomers. The facile formation of oligomers is in contrast to traditional Grignard reagents, which favor monomeric formulations in ether solvents. Finally,

despite the unusual placement of five or ten contiguous magnesium substituents about a metallocene skeleton, initial studies suggest that the permagnesiased ruthenocenes react like typical organomagnesium reagents. Thus, the complete range of reactivity associated with Grignard reagents and diorganomagnesium compounds may be expected for permagnesiased cyclopentadienyl complexes and aromatic compounds. The above predictions are being investigated in our laboratory.

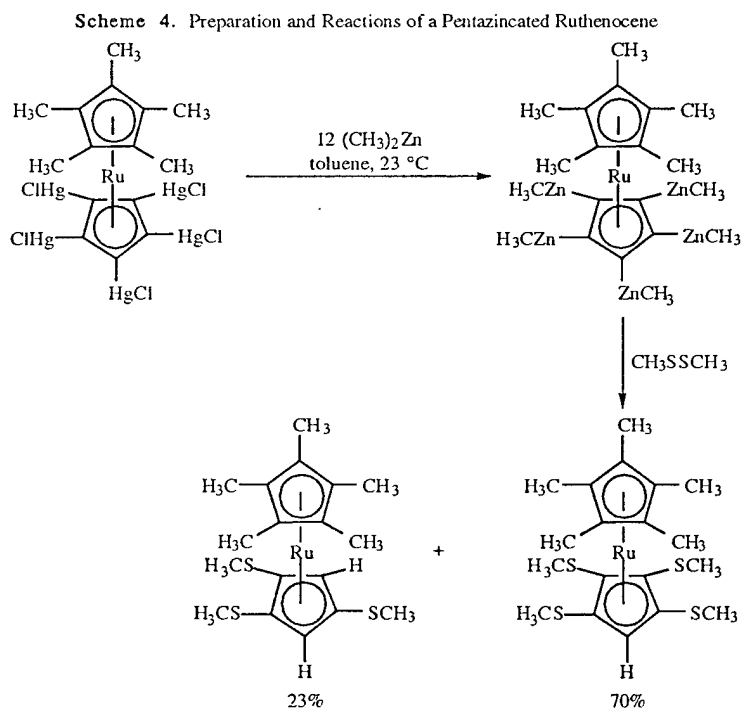
Peraluminated Cyclopentadienyl Complexes. Treatment of pentakis(chloromercurio)(pentamethyl)ruthenocene with trimethylaluminum (12 equiv) in hexane at ambient temperature led to the formation of a yellow solution containing pentakis(dimethylalumino)pentamethylruthenocene (Scheme 3). While the aluminated complex is easily isolated, its ^1H and ^{13}C NMR spectra are exceptionally complicated and have defied analysis so far. However, it can be hydrolyzed to pentamethylruthenocene and is brominated to afford



pentabromopentamethylruthenocene. These reactions are excellent evidence for the formulation of a pentaaluminated species. A particularly noteworthy reaction is that with dimethyl disulfide. Treatment with dimethyl disulfide affords pentamethyl(tetra-kis(thiomethyl))ruthenocene (40%) and pentamethyl(tris(thiomethyl))ruthenocene (20%). By contrast, treatment of pentakis(chloromagnesio)pentamethylruthenocene with dimethyl disulfide affords a mixture of the monothiomethyl and dithiomethyl derivatives, while pentamethylpentalithioruthenocene affords

only pentamethylruthenocene. Thus, the synthetic utility of the pentametalated ruthenocene increases with decreasing reactivity of the carbon-metal bond. This is a useful concept that encourages further investigation of permetalated metallocenes. As a side note, treatment of the pentaaluminated ruthenocene with dimethyl disulfide in toluene gives products derived from toluene (benzyl methyl sulfide, isomers of (thiomethyl)toluene) that are consistent with the hydrogens being introduced into the thiomethyl-substituted ruthenocenes as hydrogen atoms. This implies a radical or radical ion mechanism for hydrogen abstraction.

Perzincated Cyclopentadienyl Complexes. Treatment of pentakis(chloromercuro)-pentamethylruthenocene with dimethylzinc (12 equiv) in tetrahydrofuran at -78°C afforded a solution containing pentakis(methylzinco)pentamethylruthenocene (Scheme 4). While the chemistry is still being investigated, reaction with dimethyl disulfide suggests that its reactivity may be very useful. The tri-thiomethyl (70%) and tetra-thiomethyl (23%) ruthenocenes are isolated in higher yields than possible using the aluminated ruthenocene described above. Additionally, the selectivity for the tetra-thiomethyl ruthenocene is higher than for the aluminated ruthenocene.



Fluorination Studies. It is our idea that the new permetalated ruthenocenes should react with mild electrophilic fluorinating agents to give perfluororuthenocenes. So far, all of our attempted reactions have failed to give the desired perfluorometalloenes. However, these efforts are continuing in our laboratory.

References

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- (3) Winter, C.H.; Han, Y.-H.; Heeg, M.J. *Organometallics* 1992, 11, 3169.
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- (5) Han, Y.-H.; Heeg, M.J.; Winter, C.H. *Organometallics* 1994, 13, 3009.
- (6) Kur, S.A.; Rheingold, A.L.; Winter, C.H. *Inorg. Chem.* 1995, 34, 414.
- (7) Kur, S.A.; Heeg, M.J.; Winter, C.H. *Organometallics* 1994, 13, 1865.
- (8) Bretschneider-Hurley, A.; Winter, C.H. *J. Am. Chem. Soc.* 1994, 116, 6468.
- (9) Bretschneider-Hurley, A.; Winter, C.H., manuscript in preparation.
- (10) Seneviratne, K.; Bretschneider-Hurley, A.; Winter, C.H. *J. Am. Chem. Soc.* 1996, submitted for publication.

5. Personnel Supported

Charles H. Winter	Faculty (PI)	Summer 1993, 1994, 1995
Young-Hee Han ^a	Graduate Student	Winter 1993, Fall 1993
Sally A. Kur ^b	Graduate Student	Fall 1994, Winter 1995, Summer 1995
Kapila E. Seneviratne ^c	Graduate Student	Fall 1995
Annette Bretschneider-Hurley ^d	Postdoctoral Fellow	May 1995 to present

^aU.S. permanent resident, finished Ph.D. degree in 12/93, currently working for American Scientific Products in Georgia.

^bU.S. citizen, finished Ph.D. degree in 3/96, currently seeking employment.

^cSri Lankan citizen, currently a graduate student with the PI.

^dU.S. permanent resident, currently a postdoctoral worker at Wayne State University for the PI.

6. Publications Resulting from the Project

Since 1/1/93:

1. "Decamercuration of Ruthenocene," C.H. Winter, Y.-H. Han, R.L. Ostrander, and A.L. Rheingold, *Angew. Chem., Int. Ed. Engl.* 1993, 32, 1161.

2. "Pentamercuration of Cyclopentadienylmanganese Tricarbonyl and Cyclopentadienylrhenium Tricarbonyl. Crystal Structure of Pentaiodocyclopentadienylmanganese Tricarbonyl," S.A. Kur, M.J. Heeg, and C.H. Winter, *Organometallics* 1994, 13, 1865.
3. "Permercuration of Ferrocenes and Ruthenocenes. New Approaches to Complexes Bearing Perhalogenated Cyclopentadienyl Ligands," Y.-H. Han, M.J. Heeg, and C.H. Winter *Organometallics* 1994, 13, 3009.
4. "Pentamethylpentalithioruthenocene and Decalithioruthenocene," A. Bretschneider-Hurley and C.H. Winter, *J. Am. Chem. Soc.* 1994, 116, 6468.
5. "Synthesis, Characterization, and Halogenation of Decakis(acetoxymercurio)osmocene. Crystal and Molecular Structure of Osmocene," S. A. Kur, A. L. Rheingold, and C. H. Winter, *Inorg. Chem.* 1995, 34, 414-416.
6. "Permercuration of Substituted Ferrocenes. Assessment of the Degree of Mercuration," S. A. Kur and C. H. Winter, *J. Organomet. Chem.* 1996, in press.
7. "Synthesis, Spectroscopic Characterization, and Reactivity of Ruthenocenes Bearing Pentamagnesiated Cyclopentadienyl Ligands," K. Seneviratne, A. Bretschneider-Hurley, and C.H. Winter, *J. Am. Chem. Soc.* 1996, submitted for publication (favorable reviews obtained, revised manuscript submitted 4/3/96).

7. Interactions/Transitions

a. Presentations at Meetings

1. "Approaches to Complexes Bearing Pentafluorocyclopentadienyl Ligands," Y.-H. Han and C.H. Winter, Gordon Conference, Organometallic Chemistry, Newport, Rhode Island, July 12-16, 1993.
2. "Decamercuration of Ferrocene and Ruthenocene," Y.-H. Han and C.H. Winter, 206th American Chemical Society National Meeting, Chicago, Illinois, August 22-26, 1993, Abstract INOR-65.
3. "Persubstituted Cyclopentadienyl Complexes from Permercurated Precursors," C.H. Winter, Y.-H. Han, S.A. Welch, and A. Bretschneider-Hurley, 207th American Chemical Society National Meeting, San Diego, California, March 13-18, 1994, Abstract ORG-172.
4. "Permercuration of Cyclopentadienylmanganese Tricarbonyl, Methylcyclopentadienylmanganese Tricarbonyl, and Cyclopentadienylrhenium Tricarbonyl," C.H. Winter and S.A. Kur, Central and Great Lakes Joint ACS Meeting, Ann Arbor, MI, June 1-3, 1994, Talk #255.
5. "Synthesis, Characterization, and Reactivity of Transition Metal Complexes Bearing Pentalithiocyclopentadienyl Ligands," A. Bretschneider-Hurley and C.H. Winter, Central and Great Lakes Joint ACS Meeting, Ann Arbor, MI, June 1-3, 1994, Talk #278.

6. "Synthesis and Characterization of Permetalated Cyclopentadienyl Complexes, A. Bretschneider-Hurley and C.H. Winter, XVI International Conference on Organometallic Chemistry, University of Sussex, Brighton, England, UK, July 10-15, 1994, Talk #OB.2.
7. "Synthesis and Characterization of Transition Metal Complexes Bearing Pentalithiocyclopentadienyl Ligands," A. Bretschneider-Hurley and C.H. Winter, Gordon Conference on Organometallic Chemistry, Holderness School, The Holderness, New Hampshire, July 25-29, 1994.
8. "Synthesis and Reactivity of Permetalated Cyclopentadienyl Complexes and Aromatic Molecules," C.H. Winter, A. Bretschneider-Hurley, and K.E. Reck, 208th National Meeting of the American Chemical Society, Washington, DC, August 21-25, 1994, Talk #ORGN-436.
9. "Synthesis, Characterization, and Reactivity of Pentametalated Cyclopentadienyl Complexes," C.H. Winter, 27th Central Regional Meeting of the American Chemical Society, Akron, OH, May 31-June 2, 1995, Talk #INOR-91.
10. "Synthesis and Characterization of Transition Metal Complexes Bearing Pentametalated Cyclopentadienyl Ligands," C.H. Winter, A. Bretschneider-Hurley, and K. Seneviratne, Gordon Conference on Inorganic Chemistry, Brewster Academy, Wolfeboro, New Hampshire, July 23-28, 1994.
11. "Synthesis, Characterization, and Reactivity of Ruthenocenes Bearing Pentamagnesiased Cyclopentadienyl Ligands," C.H. Winter and K. Seneviratne, 210th National Meeting of the American Chemical Society, Chicago, IL, August 20-24, 1994, Talk #INOR-73.
12. "Synthesis, Characterization, and Reactivity of Permetalated Benzene and Anisole Derivatives," C.H. Winter and S.A. Kur, 210th National Meeting of the American Chemical Society, Chicago, IL, August 20-24, 1995, Talk #INOR-475.

b. Consultative and Advisory Functions

1. National Science Foundation, Arlington, Virginia, SBIR review panel, September 18, 1995. Served on a panel review committee that evaluated 24 proposals for possible funding under the SBIR program for FY 1995.
2. Industrial consultant for Metallamics, Inc., Traverse City, Michigan and Sage Electrochromics, Inc., Piscataway, NJ.

c. Transitions

None

8. New Discoveries, Inventions, or Patent Disclosures

None

9. Honors/Awards

Career Development Chair Award, Wayne State University, 1995-1996.